
# Comment on "Unified explanation of the anomalous dynamic properties of highly asymmetric polymer blends" [J. Chem. Phys.138, 054903 (2013)]

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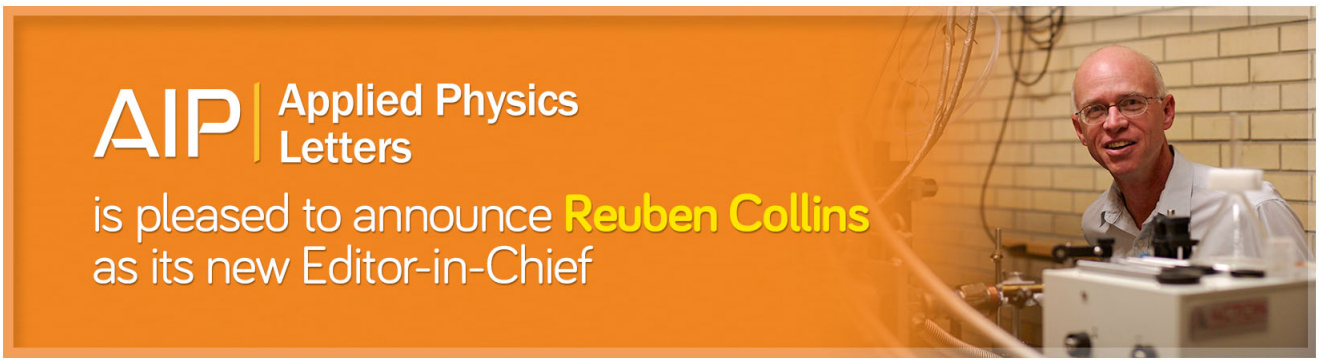

# Comment on "Unified explanation of the anomalous dynamic properties of highly asymmetric polymer blends" [J. Chem. Phys. 138, 054903 (2013)]

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In a recent paper by Ngai and Capaccioli, "Unified explanation of the anomalous dynamic properties of highly asymmetric polymer blends,"[1] the authors claimed that the so-called coupling model (CM) provides a unified explanation of all dynamical anomalies that have been reported for dynamically asymmetric blends over the last ten years. Approximately half of the paper is devoted to chain-dynamic properties involving un-entangled polymers. According to the authors, the application of the CM to these results is based on the existence of a crossover at a time $t_c \approx$ 1–2 ns of the magnitudes describing chain dynamics as, for instance, polymer segment mean squared displacement $\langle r^2(t)\rangle$ or incoherent neutron scattering function $F_s(Q, t)$. The authors claimed in their paper that "neutron scattering and molecular dynamics simulations have shown that the global self-dynamics of unentangled poly(ethylene oxide) (PEO) chains in blends with poly(methyl methacrylate) (PMMA) follow the Rouse model at times shorter than 1–2 ns, but at longer times it becomes slower and departs from the Rouse model in the dependence on time, momentum transfer, and temperature."[2,3] Being one of the authors of Refs. 2 and 3 (Refs. 24 and 25 in the paper of Ngai and Capaccioli), I am qualified to know what was actually reported in those papers. Here I will demonstrate that: (i) there is no evidence of a crossover at $t_c \approx$ 1–2 ns in the data reported in these references; (ii) the data of $\langle r^2(t)\rangle$ and the $F_s(Q, t)$ corresponding to PEO in the PMMA/PEO blends cannot be properly described by the Rouse model at $t <$ 1–2 ns. These results thereby invalidate the application of the CM to the chain-dynamic properties carried out by Ngai and Capaccioli.

First we will focus on the MD-simulation results reported in Ref. 3, which cover a rather wide dynamic range in time. Figure 1 reproduces here some of these results in the time range from 2 ps to 20 ns, which is the relevant one for this discussion (at $t <$ 2 ps only microscopic dynamics is taking place). As it was described in Ref. 3, the mean-squared-displacement of hydrogen atoms of PEO in the blend display in this dynamic range a sub-linear behavior $\langle r^2(t)\rangle \approx t^y$ with $y$-values depending on temperature [$y = 0.49$ (500 K); 0.41 (400 K); 0.36 (350 K); 0.31 (300 K)]. As can be seen in Fig. 1(a), the time dependence of $\langle r^2(t)\rangle$ does not show any crossover in the time range of 1 ns–2 ns, which is marked in the figure by the shadowed area. We arrive to the same conclusion by inspecting the corresponding incoherent scattering function, $F_s(Q, t)$, reproduced in Fig. 1(b) for a low $Q$-value of 0.3 Å$^{-1}$, which is representative for chain-dynamics behavior. On the other hand, Fig. 1(a) also shows as a continuous line the expected time dependence of $\langle r^2(t)\rangle$ for a pure Rouse behavior. It is evident that the results do not follow such a behavior even in the restricted time range $t <$ 1–2 ns. Only at high temperature (500 K), $\langle r^2(t)\rangle$ approaches Rouse-like time dependence. As it was discussed in Ref. 3, this is the expected behavior due to the fact that in the high temperature limit, the dynamic asymmetry between both blend components (PEO and PMMA in this case) should vanish. Figure 2 also shows that a Rouse-like description of $F_s(Q, t)$ ($F_s(Q, t) \approx \exp[-(t/\tau)^{0.5}]$) in the time range $t <$ 1–2 ns is just not possible (see continuous lines in the figure). It is worthy of remark that the simulations results corresponding to a generic (coarse-grained) model of asymmetric blend, which were also reported in Ref. 3, follow the same trends that those discussed above. This clearly indicates that these trends are general for asymmetric blends and not a particular case of the PMMA/PEO system.

Now we can comment on the neutron scattering results also mentioned by Ngai and Capaccioli and that were published in Ref. 2. These data also correspond to the PEO chain dynamics in blends with PMMA. In that paper, it was mentioned that the low-$Q$ incoherent scattering data corresponding to the chain dynamics of PEO in the blend, which were obtained by means of backscattering (BS) techniques, can be more or less well described by the Rouse model. However, this was not the case for the collective chain-dynamics data obtained by neutron spin echo (NSE) spectroscopy. The problem is that the dynamic range covered by BS techniques in general is extremely narrow. In the particular case of the results discussed here, it only covers about one decade in time, 0.1 ns $< t <$ 1 ns (see Fig. 2 of Ref. 2). As it was later discussed in Ref. 3, the MD-simulation results nicely show that in such a narrow range, an approximate Rouse-like description is always possible. This is shown here in Fig. 2, where the dashed line is the Rouse-like fitting curve of $F_s(Q, t)$ data at 400 K in the BS dynamic range (shadowed area). However, as the figure shows and it has been above

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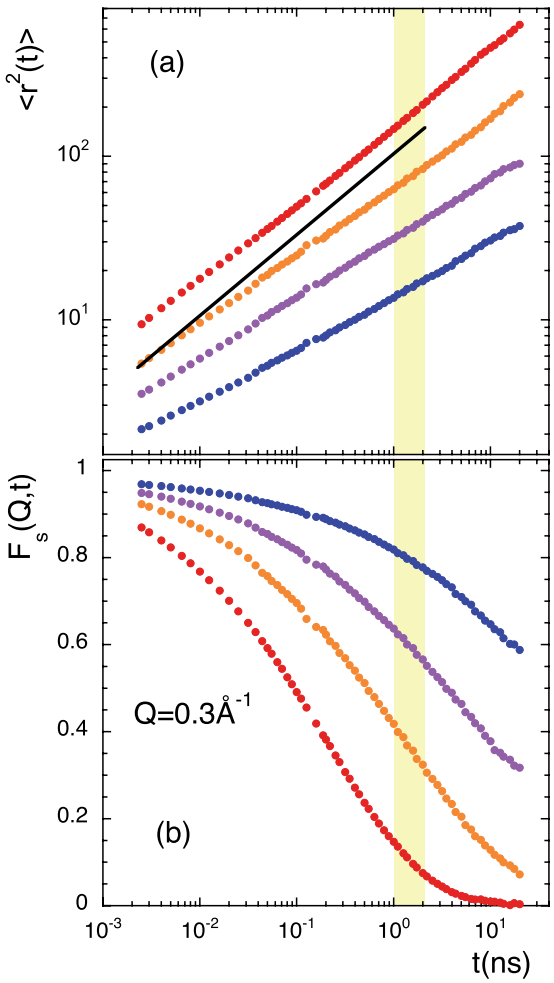


FIG. 1. (a) Mean-squared-displacement $\langle r^2(t)\rangle$ of hydrogen atoms of PEO in the blend PMMA/PEO obtained from the atomistic MD-simulations reported in Ref. 3. Temperatures from above: 500 K; 400 K; 350 K; 300 K. The continuous line is shown as an example of the behavior predicted from the Rouse model at 400 K. (b) Incoherent scattering function at $Q = 0.3$ Å$^{-1}$, corresponding to the $\langle r^2(t)\rangle$ shown in (a). The temperatures are the same that in (a) (now from below and with the same color code).

discussed, this does not imply that the data for $t <$ 1–2 ns follow the Rouse behavior. On the other hand, the data obtained by NSE covered a wider dynamic range from about 0.1 ns to 80 ns—almost three decades in time. According to the other results commented here, this explains why these data cannot be described by the Rouse model. Moreover, it is noteworthy that again they do not show any crossover at about 1–2 ns.

In conclusion, we can say that the neutron scattering and MD-simulation results reported in Refs. 2 and 3 do not give

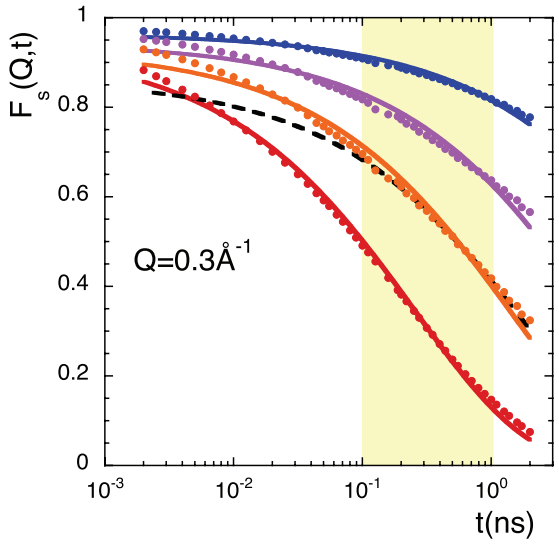


FIG. 2. The same results shown in Fig. 1(b) but now in the restricted time range 2 ps $< t <$ 2 ns. Continuous lines are fitting curves in this range to the Rouse expression (see the text). The dashed line indicates the same type of fitting but restricted to the backscattering time window mentioned in Ref. 2 (shadowed area) and for 400 K as an example.

any evidence of a crossover at $t \approx$ 1–2 ns in the magnitudes describing chain dynamics of the fast component in asymmetric blends. Thereby, in contrast to the statements of Ngai and Capaccioli, these results do not support the application of the CM carried out by these authors in Ref. 1.

Finally, it is worthy of remark that apart from the so-called random Rouse model (RRM) described in Refs. 2 and 3, and which was commented by Ngai and Capaccioli, another possible theoretical scenario, based on the generalized Langevin equation (GLE) approach, was also outlined in Ref. 3 and recently applied in Ref. 4 to successfully explain the molecular weight dependence of the Rouse time of polyisoprene (PI) in blends with poly(*tert*-butyl styrene) (PtBS). Although Ref. 4 is also commented by Ngai and Capaccioli (Ref. 29 in their paper) astonishingly they do not even mention the GLE explanation given there.

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